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(21) International Application Number: PCT/US94/07200 (22) International Filing Date: 27 June 1994 (27.06.94) (30) Priority Data: 93870123.2 28 June 1993 (28.06.93) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SURUTZIDIS, Athanasios [GR/BE]; Rue J. Vandenbroeck 13, B-1780 Wemmel (BE). FISK, Andrew, Albon [GB/BE]; Sint-Annalaan 173, B-1853 Strombeek-Bever (BE). BOUTIQUE, Jean-Pol [BE/BE]; Rue Emilo-Labarre 32, B-5800 Genbloux (BE). JONES, Roger, Jeffery [GB/BE]; Rue de Frambes 11, B-1350 Jauche (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LOW SUDSING LIQUID DETERGENT COMPOSITIONS (57) Abstract The present invention is a liquid detergent composition comprising a branched anionic surfactant. The compositions according to the present invention are low sudsing and have improved hydrophobic greasy soil removal performance.		

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LOW SUDSING LIQUID DETERGENT COMPOSITIONS

Technical Field

The present invention relates to low sudsing liquid detergent compositions.

Background of the Invention

Anionic surfactant compositions are well known in the art and are desirable components in liquid detergents due to their good cleaning ability, especially with respect to hydrophobic greasy soil removal. However, the incorporation of anionic surfactants in typical detergent compositions results in high sudsing formulations.

A number of systems have been described in the art for use in detergent compositions in order to counter act the sudsing ability of the surfactants. Such suds suppressing systems include anti-foam agents such as silicone. However, anti-foam agents have problems associated with them such as the difficulty to maintain them as a dispersion in liquid compositions. In addition silicone anti-foam agents are difficult to process and are expensive.

Therefore it is an object of the present invention to provide a liquid detergent composition comprising an anionic surfactant, said composition having a controlled sudsing profile, said composition requiring a minimum amount of conventional suds suppressing agents.

It has now been found that this can be achieved by formulating a liquid detergent composition comprising a conventional anionic surfactant in combination with an α -branched anionic surfactant.

It has unexpectedly been found that such surfactant combinations provide controlled sudsing, and simultaneously improve said compositions' performance on hydrophobic greasy soil removal.

Another advantage of the present invention is that the sudsing is reduced by the adaptation of straight chain anionic surfactants to their -branched counterparts, i.e. Guerbet anionic surfactants and thus other suds suppressing agent may only be required in minimum amounts.

Another advantage of the present invention is that the surfactants are easier to formulate due to the increased solubility of the surfactant. Furthermore, said compositions are easier to form as 'concentrated' compositions because of the almost total omission of conventional suds suppressing agents. In addition the compositions are cheaper to formulate.

Another advantage of the compositions of the present invention is that said compositions are phase stable.

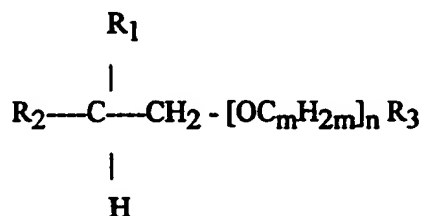
The term "Guerbet" surfactant as used herein refers to branched surfactants derived from 2-alkyl-alkanol.

Guerbet surfactants are known in the art. DE 41 11 335 discloses a low sudsing ternary surfactant mixture comprising an alkylglycoside, linear and branched secondary dialkylethersulphates and sulphate and sulphonate anionic surfactants. There is no specific mention of Guerbet anionic surfactants.

WO 91/16409 discloses a liquid detergent composition comprising branched primary alkyl sulphates. There is no mention of suds suppressing properties or any specific mention of Guerbet anionic surfactants.

Summary of the Invention

The present invention is a liquid detergent composition comprising one or more of an anionic surfactant, characterized in that said anionic surfactant comprises from 1% to 99% by weight of said anionic surfactant of a compound according to the formula:

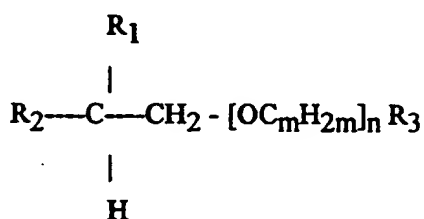


wherein R₁ is a C₃-C₂₂ alkyl group, R₂ is a C₃-C₂₂ alkyl group, m is 2, 3 or 4, n is between 0 and 14 and R₃ is a sulphate or a sulphonate.

All weights ratios and percentages are given by the weight of the total composition unless otherwise stated.

Detailed Description of the Invention

The detergent compositions according to the present invention comprise an anionic surfactant, characterized in that said anionic surfactant comprises from 1% to 99% by weight of said anionic surfactant of a compound according to the formula:



herein after referred to as Guerbet anionic surfactant. Said Guerbet anionic surfactants are low sudsing due to the β -branching. The compositions of the present invention require only a minimum amount of other suds suppressing agents. Said amount as used herein being an amount less than that used in conventional liquid detergents comprising anionic surfactants.

According to the present invention R_1 is a C_3 - C_{22} , preferably a C_3 - C_{10} , more preferably a C_3 - C_8 alkyl group.

Said R_1 alkyl group may be linear or branched, saturated or unsaturated. R_2 is a C_3 - C_{22} , preferably a C_6 - C_{14} , more preferably a C_6 - C_{12} alkyl group. Said R_2 alkyl group may be linear or branched, saturated or unsaturated. n is between 0 and 14, preferably between 0 and 7, more preferably between 0 and 5. R_3 is a sulphate or a sulphonate or mixtures thereof.

The Guerbet anionic surfactant is typically present at levels from 1 to 70%, preferably from 5 to 50%, more preferably from 5 to 25% by weight of the total detergent composition.

According to the present invention the compositions may further comprise non Guerbet anionic surfactants. Suitable anionic surfactants are selected from the group of sulphates and sulphonates. The like anionic surfactants are well known in

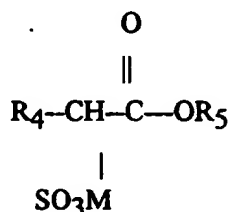
the detergent art and have found wide application in commercial detergents. Preferred anionic sulphates and sulphonates have in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms. Examples of such preferred anionic surfactants are the reaction products obtained by sulphating C₈-C₁₈ fatty alcohols derived from e.g. tallow oil, palm oil, palm kernel oil and coconut oil; alkyl benzene sulphonates wherein the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulphonates; ether sulphates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulphates and sulphonates; water soluble salts of paraffin sulphonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulphonated olefin surfactants as more fully described in e.g. US-A 3 332 880 can also be used. The neutralizing cation for the anionic synthetic sulphonates and/or sulphates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium.

A suitable anionic synthetic surfactant component herein is represented by the water soluble salts of an alkylbenzene sulphonic acid, preferably sodium alkylbenzene sulphonates, preferably sodium alkylbenzene sulphonates having from about 10 to 15 carbon atoms in the alkyl group.

Another anionic surfactant suitable for use herein can be alkyl alkoxyated sulphate surfactants. Alkyl alkoxyated sulphate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxylalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₁₈ alkyl or hydroxylalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and 3, and M is H or a cation which can be for example a metal cation (e.g. sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulphates as well as alkyl propoxylated sulphates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and those derived from alkanolamines, eg. monoethanolamine, diethanolamine and triethanolamine. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulphate (C₁₂-C₁₈E(1.0)M), C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulphate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulphate (C₁₂-C₁₈E(3.0)M), C₁₂-C₁₈ alkyl

polyethoxylate (4.0) sulphate ($C_{12}-C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Another type of anionic surfactant suitable for use herein are alkyl ester sulphonate, which can be synthesized according to known methods disclosed in the technical literature. For instance, linear esters of C_8-C_{20} carboxylic acids can be sulphonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm and coconut oils. The preferred alkyl ester sulphonate, comprise alkyl ester sulphonates of the structural formula



wherein R_4 is a C_8-C_{20} hydrocarbyl, preferably an alkyl or combination thereof. R_5 is a C_1-C_6 hydrocarbyl, preferably an alkyl or combination thereof and M is a soluble salt forming cation. Suitable salts include metal salts such as sodium, potassium and lithium salts and substituted or unsubstituted ammonium salts, such as methyl-, dimethyl-, trimethyl and dimethyl piperdinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine and triethanolamine. Preferably R_4 is $C_{10}-C_{16}$ alkyl and R_5 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulphonates wherein R_4 is $C_{14}-C_{16}$ alkyl.

When included herein, the non-Guerbet anionics are present at levels from 1% to 40%, preferably from 3% to 20%, by weight of the total detergent composition.

The rest of the liquid detergent composition according to the present invention is made of conventional detergency ingredients, i.e. water, surfactants, builders and others.

The liquid detergent compositions herein may additionally comprise as an optional ingredient from 1% to 50%, preferably from 5% to 25% of an organic surface-active agent selected from nonionic, cationic and zwitterionic surface active agents and mixtures thereof.

The nonionic surfactants suitable for use herein include those produced by condensing ethylene oxide with a hydrocarbon having a reactive hydrogen atom, e.g., a hydroxyl, carboxyl, or amido group, in the presence of an acidic or basic catalyst, and include compounds having the general formula $RA(CH_2CH_2O)_nH$ wherein R represents the hydrophobic moiety, A represents the group carrying the reactive hydrogen atom and n represents the average number of ethylene oxide moieties. R typically contains from about 8 to 22 carbon atoms. They can also be formed by the condensation of propylene oxide with a lower molecular weight compound. n usually varies from about 2 to about 24.

A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 4 to 10 moles of ethylene oxide per mole of fatty alcohol. Suitable species of this class of ethoxylates include: the condensation product of C_{12} - C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of alcohol; the condensation product of narrow cut C_{14} - C_{15} oxo-alcohols and 3 to 9 moles of ethylene oxide per mole of fatty(oxo)alcohol; the condensation product of a narrow cut C_{12} - C_{13} fatty(oxo)alcohol and 6.5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C_{10} - C_{14} coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 4 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight%) is frequently found in commercial oxo alcohols.

The compositions according to the present invention contain from 0% to 30% preferably from 0% to 10% of nonionic surfactants.

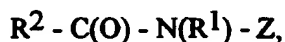
Suitable cationic surfactants for use herein include quaternary ammonium compounds of the formula $R_1R_2R_3R_4N^+$ where R_1 , R_2 and R_3 are methyl groups, and R_4 is a C_{12-15} alkyl group, or where R_1 is an ethyl or hydroxy ethyl group, R_2 and R_3 are methyl groups and R_4 is a C_{12-15} alkyl group. The compositions according to the present invention contain from 0% to 20% of cationic surfactants.

Another optional ingredient are zwitterionic surfactants. Suitable zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and

sulphonium compounds in which the aliphatic moiety can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 24 carbon atoms and another substituent contains, at least, an anionic water-solubilizing group. Particularly preferred zwitterionic materials are the ethoxylated ammonium sulphonates and sulfates disclosed in U.S. Patents 3,925,262, Laughlin et al., issued December 9, 1975 and 3,929,678, Laughlin et al., issued December 30, 1975. The compositions according to the present invention contain from 0% to 20% of zwitterionic surfactants.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl or hydroxy alkyl moiety of from about 8 to about 28 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups, containing from 1 to about 3 carbon atoms which can optionally be joined into ring structures.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula $R-CH(COOH)CH_2(COOH)$ wherein R is C_{10-20} alkyl or alkenyl, preferably C_{12-16} , or wherein R can be substituted with hydroxyl, sulfo sulphonyl or sulphone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Suitable fatty acid builders for use herein are saturated or unsaturated C_{10-18} fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

A preferred builder system for use herein consists of a mixture of citric acid, fatty acids and succinic acid derivatives described herein above. The builder system according to the present invention preferably represents from 0% to 30%, preferably from 5% to 25% by weight of the total composition.

The compositions according to the invention preferably comprise enzymes. Suitable enzymes for use herein are protease, lipases, cellulases and amylases and mixtures thereof. The compositions according to the present invention may also comprise an enzyme stabilizing system. Any conventional enzyme stabilizing system is suitable for use herein, and preferred enzyme stabilizing systems are based on boric acid or derivatives thereof, 1,2-propanediol, carboxylic acids, and mixtures thereof. The compositions according to the present invention contain from 0% to 15%, more preferably from 0% to 5% of enzymes.

The compositions herein can contain a series of further, optional ingredients. Examples of the like additives include solvents, alkanolamines, pH adjusting agents, suds suppressing agents such as silicones and 2-alkyl-alkanol, opacifiers, agents to improve the machine compatibility in relation to enamel-coated surfaces, perfumes, dyes, bactericides, brighteners, soil release agents, softening agents and the like.

The compositions according to the present invention can be formulated as conventional liquid detergent compositions or, as an alternative as so-called "concentrated" liquid detergent compositions, i.e. liquid detergent compositions comprising less than 30% by weight of water.

Whilst the detergent compositions of the invention are of particular utility in machine washing processes, most especially when formulated as heavy duty liquid laundry detergent compositions, they may also be usefully be employed in other washing processes where suds control is of importance. In particular the compositions of the invention may be usefully be formulated as machine dishwashing compositions, especially granular machine dishwashing compositions.

EXAMPLES

The following compositions are made by combining the following ingredients in the listed proportions.

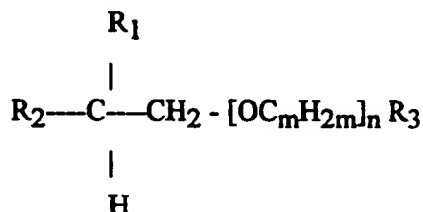
<i>Composition in %</i>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
-Branched C ₁₂ -C ₁₅ alkyl sulphate*	5	10	20	25	-
-Branched C ₁₂ -C ₁₅ alkyl 3EO sulphate**	-	-	-	-	25
Linear C ₁₂ -C ₁₄ alkyl sulphate	15	10	1	1	-
Fatty alcohol (C ₁₂ -C ₁₅) ethoxylate	12	12	12	12	12
Fatty acid	10	10	10	10	10
Oleic acid	4	4	4	4	4
Citric acid	1	1	1	1	1
Diethylenetriaminepenta-methylene phosphonic acid	1.5	1.5	1.5	1.5	1.5
Monoethanolamine	3	3	3	3	3
Propanediol	1.5	1.5	1.5	1.5	1.5
Ethanol	10	10	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7	0.7	0.7
Thermamyl ^R 300 KNU/g	0.13	0.13	0.13	0.13	0.13
Carezyme ^R 5000 CEVU/g	0.014	0.014	0.014	0.014	0.014
Protease 40mg/g	1.8	1.8	1.8	1.8	1.8
Lipolase ^R 100 KLU/g	0.14	0.14	0.14	0.14	0.14
Endoglucanase A 5000 CEVU/g	0.53	0.53	0.53	0.53	0.53
Water & Minors (suds suppressors, perfume)	up to 100 parts				
pH adjusted to 7.5-9 with NaOH					

* Lial C₁₂-C₁₅ alkyl sulphate Na salt prepared from the Lial C₁₂-C₁₅ alcohol available from Enichem

** Lial C₁₂-C₁₅ alkyl ethoxy sulphate Na salt prepared from the Lial C₁₂-C₁₅ alcohol 3 times ethoxylated available from Enichem

What is Claimed is:

1. A liquid detergent composition comprising one or more of an anionic surfactant said anionic surfactant having the formula :



wherein R_1 is a C_3 - C_{22} alkyl group, R_2 is a C_3 - C_{22} alkyl group, m is 2, 3 or 4, n is between 0 and 14 and R_3 is a sulphate or a sulphonate.

2. A liquid detergent composition according to claim 1, wherein R_1 is preferably a C_3 - C_{10} alkyl group and R_2 is preferably a C_6 - C_{14} alkyl group, n is between 0 and 7 and R_3 is a sulphate or a sulphonate.
3. A liquid detergent composition according to claim 1, wherein R_2 is C_6 - C_{12} alkyl group, R_1 is C_3 - C_8 alkyl group and R_3 is a sulphate.
4. A liquid detergent composition according to any of the preceding claims, wherein said anionic surfactant is present at levels from 1 to 70%, preferably from 5 to 50%, more preferably from 5% to 25% by weight of the detergent composition.
5. A liquid detergent composition according to any of the preceding claims, further comprising an anionic surfactant selected from alkyl sulphates, alkylbenzene sulphonates, alkyl alkoxyated sulphates and alkyl ester sulphonates.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07200

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61K 7/50, 7/06

US CL :252/549, 550, 553, 555, 556

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/549, 550, 553, 555, 556

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: Search terms: guebert, 2-alkyl-alkanol, sulphate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,183,601 (JISAI ET AL), 02 FEBRUARY 1993. SEE CLAIMS AND EXAMPLES I-IV.	1-3
Y	US, A, 5,015,414 (KAMEGAI ET AL), 14 MAY 1991. SEE ENTIRE DOCUMENT.	1-3
Y	US, A, 4,931,216 (IGARASHI ET AL), 05 JUNE 1990. SEE ENTIRE DOCUMENT.	1-3,6,7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
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Date of the actual completion of the international search

30 AUGUST 1994

Date of mailing of the international search report

14 NOV 1994

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/07200

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-5
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.